

Microwave Regeneration of Adsorbents and Plasma Conversion of VOC's

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Abstract

A microwave torch was used in a study of the destruction efficiency of the volatile organic compounds trichloroethene and toluene that were chosen to represent the classes of chlorinated hydrocarbons and aromatic hydrocarbons respectively. These compounds were added to a flow that contained argon as a carrier gas in addition to oxygen and steam. The oxygen was necessary to ensure that undesirable by-products were not formed in the process. Microwave powers of 500W to 600W were found to be sufficient to achieve the destruction of the test compounds down to the detection limits of the gas chromatograph that was used in the analysis. Samples of the post microwave gases were collected on a sorbent tube for the analysis of dioxins and other by-products. No hazardous by-products were detected when sufficient oxygen was added to the flow. The destruction efficiency improved with the addition of steam to the flow that passed through the torch. The microwave torch system is an effective control strategy for volatile organic compounds and is ideally suited for combined systems in which steam regenerated sorbent beds are used for the concentration of dilute streams of pollutants.

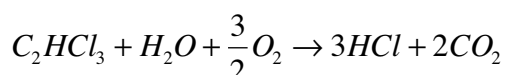
Executive Summary

A microwave-induced, steam/oxygen (H₂O/O₂) plasma, was operated at atmospheric pressures to determine the feasibility of destroying two representative VOCs of concern: trichloroethene (TCE) - a chlorinated solvent, and toluene (TOL) - a common volatile organic compound (VOC) found in gasoline, coatings and other consumer products. This plasma process can be coupled with adsorbent technology by providing steam as the fluid carrier for desorbing the VOCs, thereby excluding nitrogen gas and avoiding NO_x formation by the plasma.

The following major objectives of this study were accomplished:

- 1) To study the technical feasibility of destroying VOCs from gas streams by using a commercially available microwave plasma torch
- 2) To examine byproducts of destruction of TCE and toluene by the microwave plasma process

In a H₂O/O₂ plasma process, H₂O serves as both a source of oxygen and/or hydrogen. Oxygen was added as dictated by stoichiometric requirements of a particular oxidation reaction. For example, in the case of one TCE (C₂HCl₃) molecule, one H₂O molecule and 3/2 of an O₂ molecule are required:



to produce hydrochloric acid (HCl) and carbon dioxide (CO₂) as stable products.

Chlorine that is present in waste materials is conveniently sequestered as HCl – the Cl-atom is bonded to an H-atom, effectively removing it from participation in further reactions, except at very high temperatures. Dechlorination of wastes is an important first step in reducing the toxicity of remediation byproducts through the prevention of formation of compounds such as tetra-chloro-dibenzo-dioxin (TCDD). During this study, formation of HCl was determined by measurement of chloride ions. The destruction efficiency of the parent compound and the formation of chlorinated byproducts were measured.

Varying blends of argon (Ar), steam, and either TCE or TOL were passed through the microwave-plasma reactor with and without the presence of oxygen. In the presence of at least a stoichiometric amount of oxygen and at an input power of 400W or above, no detectable chlorinated byproducts were observed, and the destruction efficiency of TCE was greater than 99.99%. In the absence of oxygen, chlorinated byproducts were observed, including formation of trace amounts of chlorinated dioxins. In the case of toluene, destruction efficiencies greater than 99.96% were observed at microwave input power levels of 500W.

The presence of steam had an important impact on the effectiveness of the microwave destruction process. Above 10% steam in the gas mixture, destruction efficiency was essentially complete (> 99.99%). The effect of steam is consistent with the observation of

Barat and Bozzelli who observed that at the temperatures of the microwave plasma, thermodynamics favors the dechlorination of chlorinated hydrocarbons. Thus both oxygen and steam are required in order to produce the desired products and avoid byproducts.

Although the feasibility of applying a microwave-steam plasma for VOC destruction has been demonstrated, the economic viability still needs to be determined. However, the low input power requirements to produce an effective plasma (about 600W), is promising and is in the range of consumer microwave magnetrons and power supplies. Therefore, the cost of the power source(s) should not be prohibitive. Additional studies of the maximum water concentration that can be utilized before overheating the plasma torch region should be undertaken.

INTRODUCTION

As of 1997, total U. S. emissions of volatile organic compounds (VOCs) had fallen to an estimated 19×10^6 tpy (tons per year) while total NO_x emissions continued to rise to about 24×10^6 tpy¹. Among VOC categories, solvent usage increased to roughly 6.5×10^6 tpy². Of especial concern are those compounds that are toxic air contaminants (TAC), or that may produce toxic by-products while undergoing capture and treatment. Chlorinated solvents, chlorofluorocarbons and sulfur hexafluoride fall into such a category because of their higher activation energies and low biodegradability under oxidative conditions. In terms of millions of U.S. tons of carbon equivalents, i.e., a measure of greenhouse gas potential, an increase of about 67% (16×10^6 tpy) has occurred in the emissions of HCFCs, PFCs, and SF_6 during the decade of the 1990's². Although increases in emissions have occurred, concentrations of emitted streams may actually be decreasing because of improved production methods or capture of these pollutants. Control costs generally increase as concentrations decrease, e.g., the cost of catalytic incineration of VOCs increases from about \$5,000/ton to \$50,000/ton for a compound such as benzene as its concentration drops from 100 ppm_v to 10 ppm_v resulting in even the least costly of combustion control measures impractical for low concentration streams. Control costs for NO_x range from roughly less than about \$1000/ton for advanced burner technologies to over \$5,000/ton for exhaust gas treatments³. Development of efficient control strategies for low concentrations of these compounds while avoiding NO_x formation is highly desirable.

BACKGROUND

Conventional methods for removing volatile organic compounds (VOC's) from gas streams include absorption, adsorption, condensation, and incineration (including thermal and catalytic). Among these technologies, adsorption is an efficient and economical method for moderate to low concentration streams. Nevertheless, adsorbates (such as VOCs) must be removed periodically after they saturate the adsorbents (e.g., activated carbon or zeolites) and require further treatment.

There are two conventional regeneration methods: steam and hot gas regeneration. The former requires a steam generation facility while leaving the adsorbent bed wet with condensate, thus requiring that time and equipment be available to dry out the bed before its reuse. Moisture in the condensate can also lead to undesirable chemical reactions between the VOCs and bed materials. Regeneration with a hot gas is accomplished by heating the adsorbent (and adsorbate) to a temperature sufficient to desorb the adsorbate. The flow of hot gas not only heats the adsorbent, but also purges the adsorbate as it is desorbed resulting in a lower final concentration factor. Effective adsorbents also create a problem in regeneration, since generally, the more effective the adsorbent the more difficult it is to remove the adsorbate. Thus, a long regeneration time and large purge gas volumes are required. Moreover, the heating requirements are large since not only the adsorbent, but also the adsorbent support, the adsorbent column, associated conduits and the purge gas itself often must be heated. If a higher temperature purge gas was used, the desorption could be more rapid, but thermal degradation could yield undesirable

intermediate by-products and shorten the life of the adsorbent reducing its capacity. In the case of activated carbon the potential for a fire exists.

Microwave regeneration utilizes "dielectric heating" which eliminates many of the above drawbacks and provides benefits unobtainable with conventional regeneration. In the microwave regeneration process, heat is generated internally, i.e., within the adsorbent bed either by heating the adsorbate directly and/or the adsorbent. It does not need to be conveyed through a fluid; therefore a minimal amount of purge gas is used and large concentration factors can be obtained. Minimal heating of ancillary mass occurs, reducing overall energy requirements and cooling time. As a result, a microwave regeneration process makes it possible to desorb VOCs from adsorbents rapidly and efficiently. In addition, the microwave system can be used for the destruction of the desorbed waste stream.

Microwave heating is fundamentally different from conventional heating processes. As a result of internal and volumetric heating, the thermal gradients and the flow of heat in microwave-regenerated adsorbents differ from those of adsorbents regenerated by conventional heating, such as steam, or hot air regeneration, i.e., if the adsorbent is a microwave-transparent material, it is heated indirectly by the microwave-active adsorbate within the internal pore structure. Consequently, microwave processing makes it possible to regenerate adsorbents very rapidly and uniformly.

Microwaves are electromagnetic waves that have a frequency range of 0.3 to 300 GHz and correspond to wavelengths ranging from 1 m to 1 mm. Microwaves also obey the laws of optics and can be transmitted, absorbed, or reflected, depending on the material type. Metals are opaque to microwaves and thus are good reflectors. A requirement for effective transfer of energy throughout an adsorbent bed is that the adsorbent be a low loss material. We have used two types of adsorbents in prior work, hydrophobic zeolites (Degussa and UOP) and polymeric adsorbents (DOW and Nobel Chematur). Both are low loss materials that are relatively transparent to microwaves. Nevertheless, many VOC adsorbates can directly absorb microwave energy, while others are transparent.

The absorption of microwave energy is dependent upon the adsorbate molecular polarizability P , which in turn depends on dielectric constant, ϵ , molecular weight M , and density, ρ

$$P = \frac{(\epsilon+1)}{(\epsilon+2)} \frac{M}{\rho} \quad (1)$$

Polarizability is comprised of two terms, the temperature independent optical shift, and the orientation polarization P_o , representing the effect of the permanent dipole moment. It follows that

$$P_o = \frac{4}{3} \pi N \frac{\mu^2}{3kT} \quad (2)$$

where N is the Avogadro's number, T is the temperature, μ is the dipole moment, and k is the Boltzmann constant. The larger the molecular polarizability, the larger is the effect of a high frequency field. Dipoles follow the rapid changes of external field polarity, resulting in rotations and vibrations that generate heat. Most compounds will be directly

affected by short wavelengths, except strictly symmetrical compounds, such as hexane, benzene, and tetrachloroethane, which are unable to move their functional groups (their dipole moment equals zero). For these compounds, our earlier experiments⁴ have shown that the addition of water vapor can aid the regeneration process because water vapor can absorb microwave energy far more rapidly and effectively, thus heating these compounds indirectly. Unlike steam regeneration, however, condensation of the water vapor in the adsorbent bed is unnecessary as a means of heating the bed, thus avoiding aqueous phase reactions and shortening heating and drying cycles.

Based on preliminary experiments, Di and Chang⁴ showed that the microwave regeneration technique has the following advantages over conventional regeneration: (1) shorter regeneration time is needed, (2) less purge gas volume is used, hence higher concentrations are obtained (3) less total energy is needed, (4) no external steam source is required, hence the system is self-contained, (5) it is possible to desorb microwave transparent adsorbates, and (6) the adsorbent cools more rapidly. Furthermore, since steam can be used as the regenerating fluid carrier, nitrogen in the air can be excluded. Thus, by coupling the process with a plasma source, toxic compounds can be efficiently destroyed without production of thermal NO_x .

Microwave technology for waste treatment

Plasma processing for environmental remediation applications is a developing technology. The primary interest in plasma processes has been in the area of combustion, due to the ability to generate extremely high temperatures, approaching 10,000 K, in the gas phase. By comparison, most chemical thermal processes, such as incineration, operate at temperatures ranging from 2000 to 2500 K. The higher temperatures attainable in a plasma process minimize the potential for the *in situ* formation of polynuclear aromatic hydrocarbons (PAH), and chlorinated dioxins and furans, that are major concerns of incineration processes. The cooling of a plasma is rapid and not conducive to molecular growth processes that yield complex molecules. However, thermal systems that are operated with air suffer from a common problem - the production of oxides of nitrogen (NO_x).

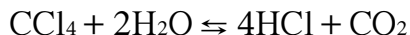
Recently there has been a growing interest in potential applications of high-frequency plasmas. For example, Wang et al.⁵ reported the use of a RF plasma system to convert dichlorodifluoromethane to methane and acetylene in a hydrogen environment. Microwave plasmas may also be applied to the remediation of off-gas streams. Microwave plasmas possess a number of advantages over plasmas generated by other types of electrical excitation which make them attractive for this application: (1) production of high ionization levels and molecular dissociation without excess heating of the contained gas; (2) construction of reaction vessels which are simple, free from contamination and less subject to damage because of the absence of internal electrodes; (3) production of little electrical interference; (4) absence of high voltages which can be easily contacted by operating personnel, i. e., absence of shock hazards; (5) potentially lower power consumption; and (6) the ability to tolerate high concentrations of water. The latter feature is particularly important because it means that energy can be fed directly into a flow with high water concentration and a stable plasma can be established.

Although the microwave plasma process has been successfully applied in the metals ⁶ and microelectronics industries ⁷, the application of microwave plasma technology to hazardous waste treatment is very limited. Bailin et al. ⁸ first investigated the decomposition of organic compounds by passage through a microwave-induced oxygen plasma. The basic idea in their study was to apply microwave discharge energy to break chemical bonds of organic compounds under reduced pressure conditions. Hertzler et al. ⁹ oxidized halocarbons with molecular oxygen directly in a low-pressure tubular flow microwave plasma discharge reactor. Although conversion of parent compounds exceeded 99.99%, a complete product analysis was not provided, and, therefore effluent toxicity could not be determined. Moreover, in the above studies, the organic compounds were introduced in liquid form into the plasma reactor. In other words, a microwave plasma was used to treat liquid organic wastes.

Researchers in Japan have been particularly active in promoting plasma technology for waste remediation. They have included microwave plasma systems in their studies. Suzuki et al. ¹⁰ investigated the use of a microwave heated oxygen plasma for the conversion of metal chlorides into oxides. The method was shown to be successful in the conversion of a wide range of metals, from transition metals to lanthanides, with results that were consistent with an equilibrium analysis. Shimizu et al. ^{11, 12} studied the decomposition of trichlorotrifluoroethane with a microwave induced argon plasma. They used SiC fibers to assist in the generation of the plasma. The plasma was operated at one atmosphere pressure with small amounts of O₂ added to ensure complete conversion of C to CO₂. Somewhat surprisingly, they found that pulsed microwave operation achieved better destruction of the waste feed than DC operation. However, the reason for this behavior was not discovered.

Chlorine that is present in waste materials is most conveniently sequestered as HCl. When Cl is bonded to H it is effectively removed from participation in all further reactions, except at very high temperatures. Ultimately, HCl can be handled readily with devices such as wet scrubbers where it can be neutralized. Dechlorination of wastes is an important first step in reducing the toxicity of remediation by-products through the prevention of formation of compounds such as tetra-chloro-dibenzo-dioxin (TCDD).

The dechlorination of these compounds is thermodynamically favored by reaction in a reducing environment. Barat and Bozzelli ¹³ showed that an overall reaction of the form



exhibited large equilibrium constants

T, K	K _p
300	3.8 x 10 ⁴³
800	7.6 x 10 ²⁵

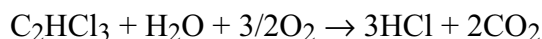
When oxygen is present in the system, O competes with Cl for bonding with H atoms. Hence, the ideal conditions for dechlorination are reducing, not oxidative. Barat and

Bozzelli used a quartz flow reactor, driven by a microwave plasma, to examine the reaction of H₂ and H₂O with chlorocarbons. Reactions with H₂ yielded non-parent chlorocarbons, low molecular weight hydrocarbons, and soot. Reactions with water yielded only carbon monoxide and carbon dioxide. The production of carbon monoxide was a necessary side effect of the stoichiometry that was used; insufficient oxygen was available to ensure complete oxidation of the available carbon. Ravindran et al.¹⁴ have shown from thermodynamic arguments that a similar dechlorination process is also possible in hydrocarbon rich environments.

MATERIALS AND METHODS

A continuous microwave generator (low ripple magnetron, 1.5 kW, 2450 MHz; Gerling Laboratory) and a resonant plasma tuner (ASTEX) were used to generate a argon/steam-based plasma. A schematic diagram illustrating the gas flow paths is shown in Fig. 1. The main components of the system consisted of a plasma reactor (AX 7200), a plasma tuner, microwave generator and microwave waveguide. Continuous microwave power from the magnetron was conducted through a waveguide to the plasma torch. The forward and reflected powers from the plasma torch could be maximized and minimized by adjusting the tuning stubs on the plasma tuner. The forward power was maintained at 600W and the reflected power was maintained below about 100 W. The plasma reactor consisted of a 1/4" O.D. ceramic tube through which the mixture to be reacted was passed, and an outer quartz tube housing.

Argon, oxygen and steam were used as gases from which a plasma was generated. The Ar was utilized as a basic carrier and reference gas, the O₂ provided stoichiometric oxidation requirements for the chlorinated hydrocarbon tested, and steam provided a reactive atmosphere containing additional hydrogen. In a H₂O/O₂ plasma process, H₂O can serve as both a source of oxygen and/or hydrogen. However, oxygen is added as dictated by stoichiometric requirements of a particular oxidation reaction. For example in the case of TCE (C₂HCl₃) one H₂O molecules and 3/2 of an O₂ molecule are required:



Steam was generated by a coiled-tubing heater and was carried by Ar gas. All plasma gas flow rates were controlled by rotameters and were introduced to the plasma torch as shown in Fig. 1. The total flow rate of gases was held constant at 10 Lpm. The proportion of steam was established by trial-and-error to obtain an intense plasma. All the lines from the flow meter to the torch were heated to prevent steam condensation.

A solvent, trichloroethene (TCE), was selected as one of the target compounds and introduced through the ceramic tube that is housed on the centerline of the plasma reactor. The other target compound was toluene (TOL). An input concentration of 1700 ppm of TCE was chosen for two reasons: ease of generation of vapor in this concentration range, and similarity to the typical concentrations expected from a sorbent bed system that might be used to concentrate a dilute stream of VOC. Similar reasoning applied to the choice of TOL input concentrations of 500 and 800 ppm.

Destruction and removal efficiencies (DRE) for TCE and TOL were calculated from measured concentrations remaining and the known flow rates to determine the effectiveness of the steam plasma. The effluent gas from the plasma reactor was passed through two traps. The first trap consisted of a coiled water concentrator and an Erlenmeyer flask, in which the most of the steam was condensed. A second back-up trap was used to condense the remaining water vapor. Gas samples were collected with high efficiency on an adsorbent bed of Carbotrap C. A gas sampling loop and switching valve were used to inject gas samples to a Varian 6000 GC from a by-pass line exiting the second trap. Liquid samples were also collected from the first and the second traps.

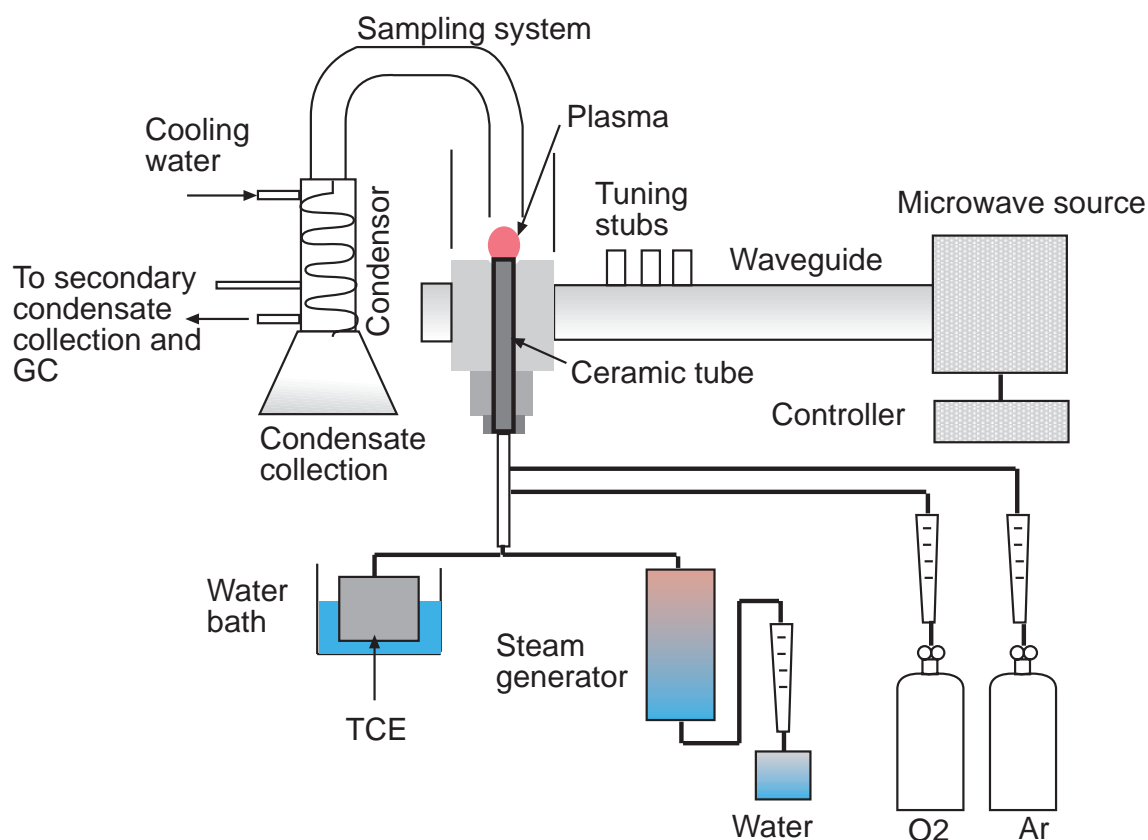


Figure 1. Microwave apparatus illustrating components: gas supplies, microwave source, resonant tuning stubs, plasma torch, steam generation and condenser system.

The reactor effluents were analyzed with an on-line Varian 6000 GC equipped with a thermal conductivity detector for TCE and TOL, and by GC/MS analysis of adsorbent tube (Carbotrap) extracts for TCE and other by-products. A specific ion meter was used to measure Cl^- concentrations in the condensate. The Carbotrap samples were Soxhlet extracted for 20 hours with dichloromethane (MeCl_2). The samples were evaporated down to 0.5 mL prior to injection into a Varian 3800 GC/MS, using a DB-5MS, 30m x 0.32 mm column. Deuterated phenanthrene and terphenyl were used as internal standards

at a concentration of 100 $\mu\text{g/mL}$ of MeCl_2 . The GC calibration curves for TCE and for TOL are shown in Figs. 2 and 3.

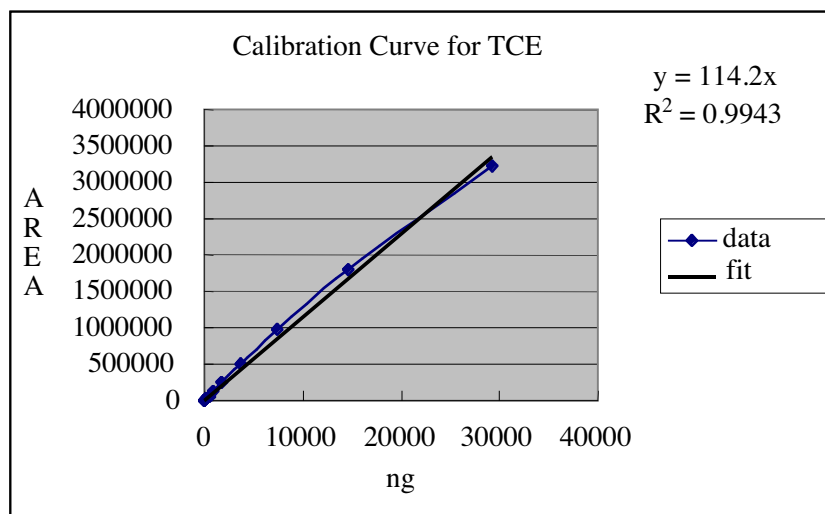


Figure 2. GC calibration for TCE.

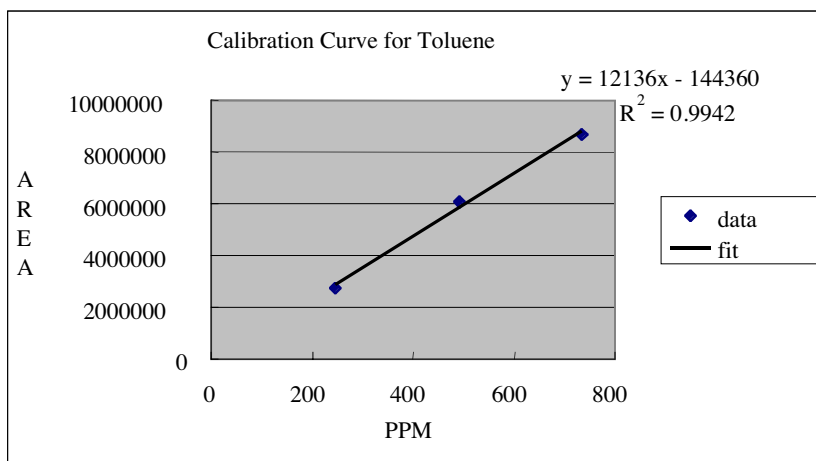


Figure 3. GC calibration for toluene.

RESULTS

The DRE for TCE was evaluated in the microwave system for a series of microwave powers at a condition of 30% steam with an O_2 flow rate of 0.5 Lpm and an argon flow rate of 6.0 Lpm. The concentration of TCE in the input flow to the plasma was 1700 ppm. The small amount of O_2 was added to ensure that sufficient O_2 was available in the system to complete the oxidation of TCE. The post-plasma gases were analyzed on a GC. The results are shown in Table 1.

Table 1. DRE and Cl⁻ ion concentration in post plasma gases at different operating powers

Power (W)	DRE (%)	Cl ⁻ (ppm)
200	58	10800
300	99.8	38700
400	>99.97	52000
500	>99.97	56200
600	>99.97	56900

Experiments were also conducted with a power of 600 W and a TCE input concentration of 1700 ppm, but with varying concentrations of steam in the plasma. The results of those tests are shown in Table 2.

Table 2. DRE at 600 W of input microwave power with varying steam concentrations

Steam fraction of flow (%)	DRE(%)
0	99.78
5	99.9
10	>99.97
20	>99.97
30	>99.97

Finally, the Carbotrap samples were analyzed on the GC/MS system for products of incomplete combustion at conditions of microwave power of 600 W with 30% steam and 1700 ppm of TCE. This analysis did not find any evidence, down to the detectable limit of dioxins or furans, demonstrating that a high DRE can be achieved without the production of other products of incomplete reaction¹. A mass spectrum of the sample, and the spectrum of a sample spiked with standards, are presented in Figs. 4 (a) and (b) respectively. The sample collected from the plasma system shows no evidence of the presence of 2,3,7,8-TCDD or its congeners.

¹ The detection limit had to be estimated because an internal dioxin standard was not used in the analysis. Using a conservative estimate of 50 pg as a detectable peak per injection, a detectable concentration of 0.2 ng/m³ of any dioxin isomer was the estimated limit. Detection of as little as 5 to 10 pg of a single dioxin isomer was possible with pure standards and it was assumed that 50 pg could be detected with the selected ion monitoring analysis applied. The detection limit corresponded roughly to a conversion of TCE to any single dioxin isomer of less than about 3×10^{-9} %. As can be seen in the chromatogram of Fig. 4b, the baseline was quite flat with essentially no identifiable peaks. For example, in Fig. 4b, at 17.9 and 21.9 minutes retention times two very small peaks eluted, corresponding to the retention times of known standards. However, reinjection and analysis of total ion chromatograms revealed that the ion fragments did not match any dioxin or furan isomer. A somewhat larger peak at 29.3 minutes did not elute with any of the standards and was also determined not to be a chlorinated dioxin or furan.

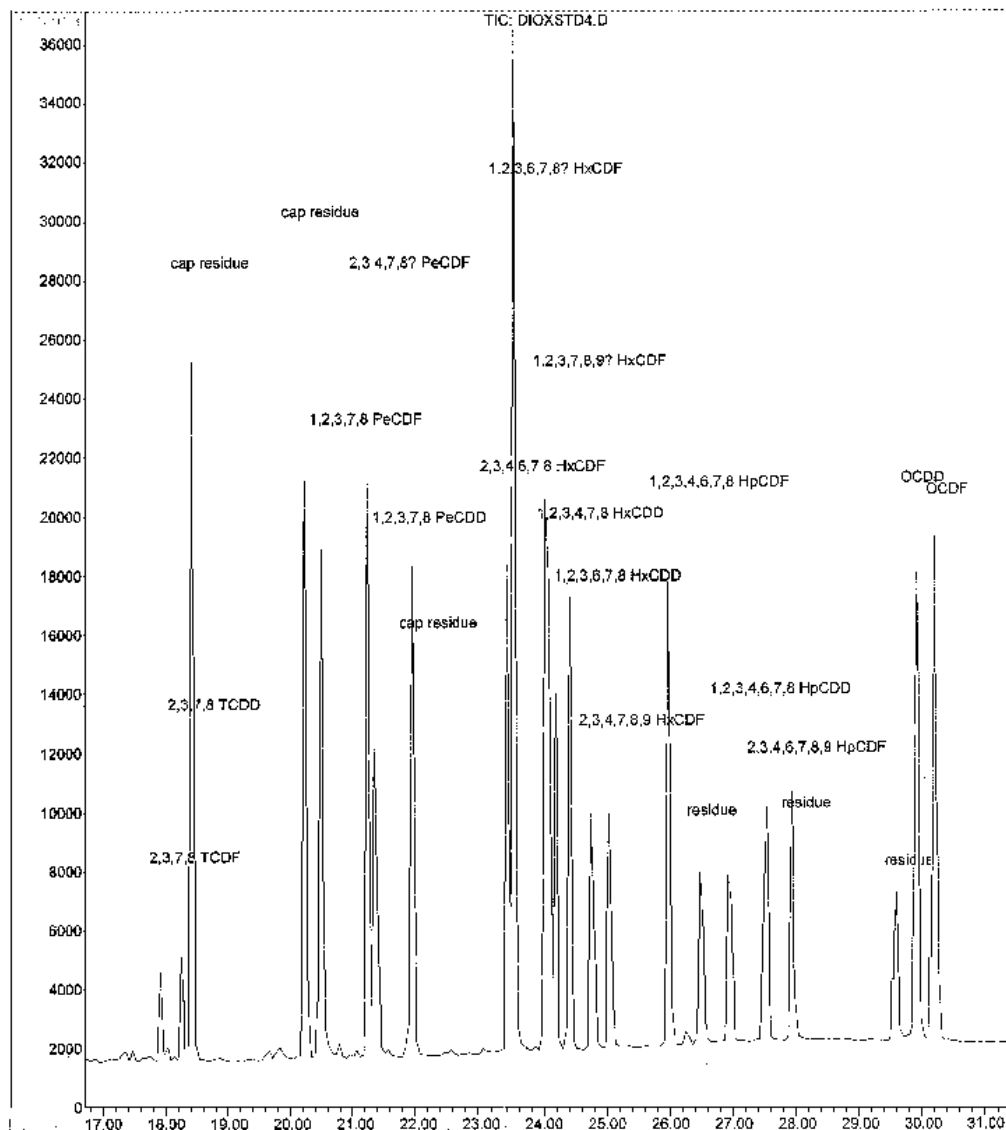


Figure 4 (a) GC-MS spectrum of dioxin and furan internal standards

File : D:\GCMSDATA\SAMPLE.D
Operator : dlu
Acquired : 10 May 2000 12:27 using AcqMethod DALE2
Instrument : GC/MS Ins
Sample Name: sorbent tube sample 5/3/00
Misc Info : sorbent tube, soxhlet 5/3/00, 2ul
Vial Number: 1

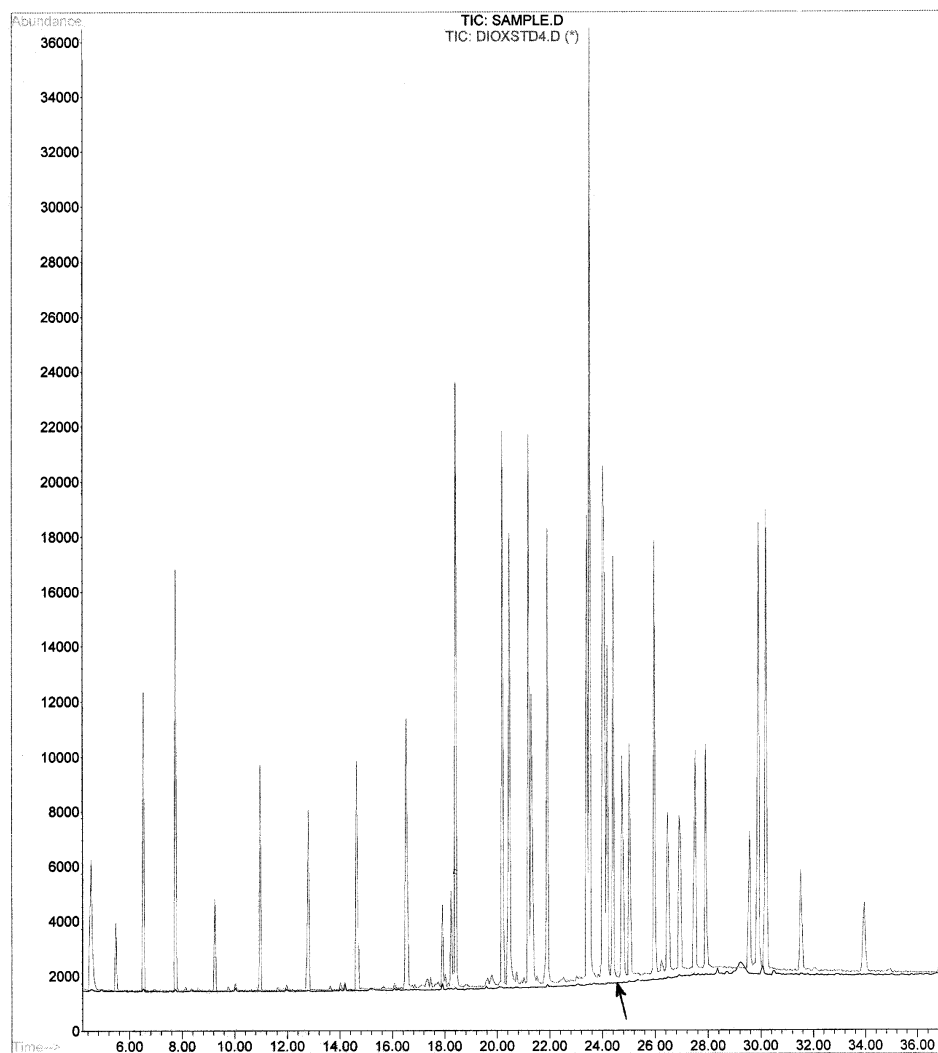


Figure 4 (b) GC-MS spectrum of internal standards overlaid by results from a sample collected above the microwave plasma (curve lying along the base of the spectrum, indicated by an arrow)

The effectiveness of the microwave system was also investigated for toluene. Two concentrations of toluene were added to the input flow. The destruction efficiency is shown in Table 3. Based upon the ability of the GC software to discriminate peak area, the detection limit for toluene was approximately 0.005% and for trichloroethene, the detection limit was 0.03%. Thus the destruction and removal efficiencies (DRE) are reported as greater than 99.99% for toluene, or greater than 99.97% for trichloroethene.

Table 3. DRE of toluene at input concentrations of 500ppm and 800ppm
Toluene 500ppm

Power(W)	DRE(%)
200	90.5
300	99.5
400	>99.99
500	>99.99
600	>99.99

Toluene 800ppm

Power(W)	DRE(%)
200	72
300	98
400	99.96
500	>99.99
600	>99.99

DISCUSSION

It is apparent that the plasma system is capable of achieving significant destruction at operating powers as low as 400 W. The chloride ion concentration is a measure of the HCl that is formed, and is a second measure of the accuracy of the sampling system and analysis. The constant Cl⁻ concentration at powers above 400 W confirms the conclusion that the majority of the input chlorine was sequestered as HCl under these conditions.

The presence of steam is seen to have an important impact on the effectiveness of the microwave destruction process. The effect of steam that is shown in Table 2 is consistent with the observation of Barat and Bozzelli that at the temperatures of the microwave plasma, thermodynamics favors the dechlorination of chlorinated hydrocarbons in the temperature window in which the plasma is operated. Sequestration of the Cl in the system as HCl prevents its further incorporation into hazardous by-products such as TCDD. The removal of the HCl could be readily achieved in a practical system through a condensing wet scrubber and subsequent neutralization. Note that the volume of gas that would require treatment is quite small since it consists then only of the amount of argon used to blend with the steam and the carbon dioxide from oxidation of the carbon atoms.

The hydrogen chloride and additional water are condensed in the scrubber. If there is sulfur in the waste stream, one would presumably remove sulfur dioxide and sulfuric acid with an alkaline scrubbing solution.

The microwave system was equally as effective with a non-chlorinated aromatic hydrocarbon (toluene) as it was with the chlorinated aliphatic compound. Once again, input power levels greater than 400 to 500W were necessary to ensure complete destruction. An analysis of heavier polynuclear aromatic hydrocarbons (PAH) in the post-plasma effluent stream was not undertaken in this case due to limited personnel resources for the project. Two tests to screen for the presence of chlorinated dioxins as byproducts of TCE destruction were performed by GC/MS on a Carbopak C sorbent trap. Results from those analyses indicate that in the absence of stoichiometric oxygen addition, a trace dioxin was detected. In the case when stoichiometric oxygen was added, no detectable dioxins were observed (LOD approximately 0.2 ng/m³).

From the power consumption and the TCE feed-rate into the plasma torch, the energy used to destroy TCE was estimated to be 300 kcal per gram of TCE. Assuming a power cost for electricity of \$0.10/kW-hr, the power cost alone for the plasma torch system was about \$35/kg of TCE or \$3500/metric ton of TCE. This does not take into account the system capital costs which would need to include an adsorbent bed system and microwave generators and pressure losses through the system. Thus, while the costs do not appear prohibitive, they are substantial and appear to be comparable to the operating costs of a catalytic system.

SUMMARY AND CONCLUSIONS

Preliminary tests of the microwave plasma system have shown that this is a feasible technology for the treatment of waste streams that include chlorinated hydrocarbons and non-chlorinated hydrocarbons. The prototype system that was tested at UC Davis was shown to be very successful in destroying trichloroethene and toluene. Destruction was achieved with acceptably moderate power levels supplied to the microwave torch and yet complete destruction was achieved with microwave powers of the order of 500 to 600 W. It was found to be important to maintain the correct stoichiometry in the mixture. To this end, oxygen needed to be added to the flow to ensure that toxic byproducts were not formed. Sampling onto a sorbent tube, followed by subsequent solvent extraction and analysis on a mass spectrometer, revealed that with sufficient oxygen no chlorinated dioxins or furans, or other hazardous poly aromatic hydrocarbons were formed. Steam was also shown to be an important factor in the destruction process. An increasing fraction of steam in the flow led to improved destruction efficiencies. This is consistent with a thermodynamic analysis that showed that the dechlorination of chlorinated hydrocarbons is quite efficient in the temperature window from about 500 to 800 degrees Celsius in which the plasma torch operates. The successful demonstration of microwave destruction suggests that a combined system, with a sorbent bed followed by steam desorption and microwave destruction, could be put into practice for real-world systems designed to control dilute streams of volatile organic compounds. The economics of the system have not been analyzed, but the moderate power levels that are required suggest that the economics may very well be favorable.

RECOMMENDATIONS

Some additional tests and avenues for research are suggested by the preliminary results that are reported here. A very limited range of concentrations, chosen to simulate the range that might be expected from an adsorbent bed, has been examined. It would be useful to examine lower concentrations to ensure that the destruction efficiency does not deteriorate as the input concentrations are reduced. It would also be useful to investigate a broader range of compounds, with a view to investigating their destruction efficiency under conditions similar to those used in the preliminary tests that have been described here.

While research on adsorbent beds was not undertaken as part of the current effort, it may be possible that the microwave energy used to regenerate the bed could also be used to power the plasma torch. That is, the adsorbent bed could be designed to be integral to the wave guide to the plasma torch region. Thus if the energy absorbed in the bed is relatively small compared to the total power generated, e.g., by using a microwave transparent adsorbent such as a zeolite, the transmitted power could be sufficient to both produce the steam to desorb the compounds and to produce a plasma. Additional studies with a manufacturer would be needed to incorporate these features into a design.

Ultimately, a more detailed scientific understanding of the microwave steam destruction process would be valuable, with a view to aiding in engineering analysis and, ultimately, in scale-up to devices of a practical size. It was observed that the thermal temperature of the system increased with the steam concentration. It would be desirable to understand the proportion of the input energy available for plasma formation, versus thermal heating of water molecules. Furthermore, an aerodynamically stabilized atmospheric pressure plasma reactor that prevents plasma contact with surfaces may be a desirable development. The recommended tasks could include measurements of electron densities in the plasma as a function of conditions, as well as detailed laser based measurements of concentrations of trichloroethene in the flow. It is possible to achieve the latter results by using a resonant Raman scattering technique that has been employed successfully in the combustion laboratory at UC Davis in the past. These basic data could be used as inputs to a computational model of the plasma destruction process. Such an engineering model would be very useful in designing and scaling-up the bench scale system that has been investigated.

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